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(54) **Polypropylene with free-end long chain branching, process for making it, and use thereof**
Polypropylen mit freier Langkettenverzweigung, Verfahren zur Herstellung und Verwendung davon
Polypropylène à branchement de longue chaîne libre, son procédé de fabrication et son application

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(73) Proprietor:
MONTELL NORTH AMERICA INC.
Wilmington Delaware 19850-5439 (US)

(72) Inventors:
• **Scheve, B. Joseph**
Wilmington Delaware 19808 (US)
• **Mayfield, John W.**
Wilmington Delaware 19803 (US)

• **DeNicola, Anthony J.**
Newark Delaware 19711 (US)

(74) Representative:
Brock, Peter William et al
Urquhart-Dykes & Lord
1 Richfield Place Richfield Avenue
Reading RG1 8EQ Berkshire (GB)

(56) References cited:
EP-A- 0 063 654 CH-A- 617 216
US-A- 3 143 584

• **Journal of Applied Polymer Science, Vol 11, 5**
May 1967, Marans & Zapas, pp 705-718
• **Journal of Applied Polymer Science, vol. 9, 1965,**
pp. 3661-3662

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Description

[0001] This invention resides in the chemical arts. More particularly, it relates to the chemical art having to do with synthetic resins derived from 1- or alpha olefins. Specifically, it relates to synthetic resins formed by the polymerization of propylene.

[0002] The synthetic resin formed by the polymerization of propylene as the sole monomer is called polypropylene. While "polypropylene" has been used from time to time in the art to include a copolymer of propylene and a minor amount of another monomer, such as ethylene, the term is not so used herein.

[0003] The well-known polypropylene of commerce is a predominantly isotactic, semi-crystalline, thermoplastic polymer mixture formed by the polymerization of propylene by Ziegler-Natta catalysis. In such catalysis the catalyst is formed by an inorganic compound of a metal of Groups I-III of the Periodic Table. (for example, an aluminum alkyl), and a compound of a transition metal of Groups IV-VIII of the Periodic Table, (for example, a titanium halide). A typical crystallinity is about 60% as measured by X-ray diffraction. As used herein, semi-crystalline means a crystallinity of at least about 5-10% as measured by X-ray diffraction.

[0004] Although the polypropylene of commerce has many desirable and beneficial properties, it is deficient in melt strength or strain hardening (an increase in resistance to stretching during elongation of the molten material). Thus it has a variety of melt processing shortcomings, including the onset of edge weave during high speed extrusion coating of paper or other substrates, sheet sag and local thinning in melt thermoforming, and flow instabilities in co-extrusion of laminate structures. As a result, its use has been limited in such potential applications as, for example, extrusion coating, blow molding, profile extrusion, and thermoforming.

[0005] On the other hand, low density polyethylene made by a free radical process has desirable melt rheology for applications that require melt strength or strain hardening properties. Such low density polyethylene is believed to have these properties because the polymer molecules are non-linear. The molecules are chains of ethylene units that have branches of ethylene units. This non-linear structure occurs because of typical free radical inter- and intra-molecular transfer followed by further subsequent polymerisation.

[0006] The polypropylene of commerce, however, is linear. That is, the polymer molecules are chains of propylene units without branches of propylene units. The reason is that in Ziegler-Natta catalysis secondary free radical reactions such as occur in the free radical polymerization of ethylene are highly improbable, if not non-existent.

[0007] Some effort has been made in the art to overcome the melt strength deficiency of the polypropylene of commerce.

[0008] Thus, as reflected in the US-A-4,365,044, to Liu, and cited references thereof, blending of linear polypropylene with a low density polyethylene that does have desirable melt strength or strain hardening properties, alone or with other polymeric substances, has been tried with some success. However, the blend approach involving different polymeric substances is not preferred.

[0009] Another approach to improve the melt properties of linear polypropylene is disclosed in the US-A-3,349,018. According to this patent, linear polypropylene is degraded by subjecting it in air to ionizing radiation at a total dose from 0.01 to 3 megareps (equivalent to 0.012 to 3.6 megarads, i.e. 0.00012 to 0.036 MGy), but less than a dose at which gelation is caused. This patent discloses that radiation degraded linear polypropylene can be extruded and drawn at much higher linear speeds without the occurrence of draw resonance or surging. However, as can be determined from the patent, particularly Example VI, the neck-in of the in-air radiated linear polypropylene is actually greater than the neck-in of the non-irradiated linear polypropylene. This is the opposite to the effect achieved by the present invention, and shows the different nature of the products.

[0010] As a matter of fact, there are a number of references that disclose the ionizing radiation treatment of linear polypropylene. These references, however, describe the resulting polymer either as degraded, as a result of chain scission, or as cross-linked, as a result of polymer chain fragments linking together linear polymer chains. There seems to be very little true recognition, if any, in these references of the possibility of an intermediate condition in which the product of the treatment is a polypropylene having "dangling" or free-end long branches.

[0011] One such reference is EP-A-0063654 which discloses visbreaking polypropylene by shear mixing at above melt temperature with polypropylene that has been subjected to ionizing radiation in air to form free radicals that initiate free radical chain scission throughout the entire polymer melt. The irradiated material is termed a "prodegradant", indicating its purpose as a source of free radicals for initiating chain-scission when added to non-irradiated polymer.

[0012] Another such reference is Marans and Zapas, J. Appl. Pol. Sci., 11, 705-718 (1967). This reference reports experiments in which samples of a powdered linear polypropylene in sealed glass tubes are subjected at pressure less than 0.3 millimeters of mercury (40 Pa) to electron radiation at various doses of radiation, and then heated to 175°C. to melt the irradiated polypropylene. The authors of this reference characterize the irradiated polypropylene of the samples as cross-linked. However, in connection with the instant invention, duplicative experiments and more advanced measuring techniques have indicated that Marans and Zapas had in fact obtained polypropylene with free-end long branches. On the other hand, the reference contains no disclosures of utility of the irradiated and heat treated samples.

[0013] Geymer, Die Makromolekulare Chemie, 99, 152-159, (1969 No. 2230), discloses experiments in which a linear polypropylene was subjected in a vacuum to gamma ray radiation from cobalt-60, and afterwards exposed to methyl mercaptan (to minimize oxidative degradation on exposure of the irradiated polymer to air), and then exposed to air. While the reference states that the simultaneous fracture and cross-linking result in branched molecules, no utility of the resulting propylene polymer material is disclosed. Moreover, while the reference does not disclose the dose rate of the gamma radiation, the usual dose rate from the usual cobalt-60 source is of the magnitude of 1 Mrad. (0.01 MGy) per hour. In view of work done in connection with the instant invention the extent of branching without cross-linking in the Geymer experiments, therefore, is believed have been insignificant.

[0014] This invention in one aspect comprises gel-free thermoplastic, i.e. normally solid, polypropylene, which has an intrinsic viscosity of at least 0.8 dl/g, measured in decahydronaphthalene at 135°C a branching index of less than 1, and which has strain hardening elongational viscosity, the branching index being defined by the equation:

$$g' = \frac{[IV]_{Br}}{[IV]_{Lin}} \quad \Bigg| \quad Mw$$

in which g' is the branching index, $[IV]_{Br}$ is the intrinsic viscosity of the gel-free polypropylene, and $[IV]_{Lin}$ is the intrinsic viscosity of linear polypropylene having substantially the same weight average molecular weight as the gel-free polypropylene, and strain hardening elongational viscosity being defined as meaning that, as said gel-free polypropylene in the molten state at a test temperature is drawn at a constant rate from a fixed point, the elongational viscosity increases until breaking of the elongated melt, and said breaking is by fracture.

[0015] Intrinsic viscosity, also known as the limiting viscosity number, in its most general sense is a measure of the capacity of a polymer molecule to enhance the viscosity of a solution. This depends on both the size and the shape of the dissolved polymer molecule. Hence, in comparing a non-linear polymer with a linear polymer of substantially the same weight average molecular weight, it is an indication of configuration of the non-linear polymer molecule. Indeed, the above ratio of intrinsic viscosities is a measure of the degree of branching of the non-linear polymer. A method for determining intrinsic viscosity of polypropylene is described by Elliott et al., J. App. Poly. Sci., 14, pp 2947-2963 (1970). In this specification the intrinsic viscosity in each instance is determined with the polymer dissolved in decahydronaphthalene at 135°C.

[0016] Weight average molecular weight can be measured by various procedures. However, the procedure preferably used here is that of low angle laser light scattering photometry, which is disclosed by McConnell in Am. Lab., May 1978, in the article entitled "Polymer Molecular Weights and Molecular Weight Distribution by Low-Angle Laser Light Scattering".

[0017] Elongational viscosity is the resistance of a fluid or semifluid substance to elongation. It is a melt property of a thermoplastic material, that can be determined by an instrument that measures the stress and strain of a specimen in the melt state when subjected to tensile strain at a constant rate. One such instrument is described, and shown in Fig. 1 of Munstedt, J. Rheology, 23, (4), 421-425, (1979). A commercial instrument of similar design is the Rheometrics RER-9000 extensional rheometer. Molten polypropylene of commerce exhibits elongational viscosity which, as it is elongated or drawn at a constant rate from a relatively fixed point, tends to increase for a distance dependent on the rate of elongation, and then to decrease rapidly until it thins to nothing - so-called ductile or necking failure. On the other hand, molten polypropylene of this invention, that is of substantially the same weight average molecular weight and at substantially the same test temperature exhibits elongational viscosity which, as it is elongated or drawn from a relatively fixed point at substantially the same rate of elongation tends to increase over a longer distance, and to break or fail by fracture - so-called brittle or elastic failure. These characteristics are indicative of strain hardening. Indeed, the more long chain branching the polypropylene of this invention has the greater the tendency of the elongational viscosity to increase as the elongated material approaches failure. This latter tendency is most evident when the branching index is less than 0.8.

[0018] This invention in another aspect provides a continuous process for making gel-free polypropylene having strain hardening elongational viscosity from amorphous to predominantly crystalline solid polypropylene without strain hardening elongational viscosity, which comprises:

- (1) continuously feeding said amorphous to predominantly crystalline polypropylene

(a) to an environment in which the active oxygen concentration is established and maintained at less than 15% by volume of said environment

(b) and irradiating said polypropylene in said environment with high energy ionizing radiation at a dose rate from 1 to 1×10^4 Mrad/min (0.01 to 100 MGy/min) until substantial chain scission of the amorphous content of the polypropylene has occurred without causing gelation of the polypropylene;

(2) maintaining the thus irradiated polypropylene in such an environment until significant formation of long chain branches has occurred,

(3) then treating the irradiated polypropylene while in such environment to deactivate substantially all of the free radicals present in the irradiated polypropylene, and

(4) continuously removing said irradiated polypropylene from said environment.

[0019] The linear polypropylene treated according to the process of this invention can be any normally solid, predominantly isotactic, semi-crystalline linear polypropylene. However, because the irradiation results in chain scission even though there is recombination of chain fragments to reform chains, as well as joining of chain fragments to chains to form branches, there can be a net reduction in weight average molecular weight between the starting material and the end product, the desired substantially branched polypropylene. In general, the intrinsic viscosity of the linear polypropylene starting material, which is indicative of its molecular weight, should be 1-25 dl/g, and preferably 2-6 dl/g, to result in an end product with an intrinsic viscosity of at least 0.8 dl/g, measured in decahydronaphthalene at 135°C, and preferably 0.8-25 dl/g, most preferably 1-3 dl/g. However, linear polypropylene with intrinsic viscosities higher than these general values are within the broader scope of this invention.

[0020] Results obtained in recent investigations have indicated that in the normally solid, predominantly isotactic, semi-crystalline linear polypropylene treated according to the process of this invention, the long chain free end branching is confined for the most part to the amorphous fraction of the semi-crystalline polypropylene. This fraction comprises normally solid atactic polypropylene as well as normally solid crystallizable, but not crystallized, stereoregular polypropylene. Hence, the linear polypropylene treated according to the process of this invention in its broader aspects can be normally solid amorphous polypropylene with little or no crystalline polypropylene content. Indeed, it can be normally solid amorphous polypropylene with little or no crystallizable polypropylene content, i.e., atactic polypropylene, or normally solid amorphous polypropylene with little or no atactic polypropylene content, i.e., crystallizable, but not crystallized, stereoregular polypropylene. Furthermore, this invention in its broader aspects comprises the polypropylene product resulting from the treatment of normally solid amorphous polypropylene by said process.

[0021] The linear polypropylene treated according to the process of this invention under the broadest concepts of the process can be in any physical form, for example, finely divided particles, pellets, film, and sheet. However, in preferred embodiments of the process of this invention, the linear polypropylene is in a finely divided condition with satisfactory results being obtained at an average particle size of about 60 mesh US screen size (0.25mm). In these embodiments it is a powder which commercially is referred to as flake.

[0022] The active oxygen content of the environment in which the three process steps are carried out is a critical factor. The expression "active oxygen" herein means oxygen in a form that will react with the irradiated polypropylene. It includes molecular oxygen (which is the form of oxygen normally found in air). The active oxygen content requirement of the process of this invention can be achieved by use of vacuum or by replacing part or all of air in the environment by an inert gas such as, for example, nitrogen.

[0023] Linear polypropylene immediately after it is made is normally substantially free of active oxygen. Therefore, it is within the concepts of this invention to follow the propylene polymerization and polymer work-up steps (when the polymer is not exposed to air) with the process of this invention. However, in most situations the linear polypropylene will have an active oxygen content because of having been stored in air, or for some other reason. Consequently, in the preferred practice of the process of this invention the finely divided linear polypropylene is first treated to reduce its active oxygen content. A preferred way of doing this is to introduce the linear polypropylene into a bed of the same blown with nitrogen, the active oxygen content of which is equal to or less than 0.004% by volume. The residence time of the linear polypropylene in the bed generally should be at least 5 minutes for effective removal of active oxygen from the interstices of particles of the linear polypropylene, and preferably long enough for the polypropylene to be in equilibrium with the environment.

[0024] Between this preparation step and the irradiation step, the prepared linear polypropylene should be maintained in an environment in which the active oxygen concentration is less than 15%, preferably less than 5% in a gas conveyance system, and more preferably below 0.004%, by volume of the environment. In addition, temperature of the linear polypropylene should be kept above the glass transition temperature of the amorphous fraction of the polypropylene, if any is present, and because it usually is, generally at less than about 40°C and preferably at 25°C, because of the increase in temperature of the polypropylene that occurs in the irradiation step.

[0025] In the irradiation step the active oxygen concentration of the environment preferably is less than 5% by vol-

ume, and more preferably less than 1% by volume. The most preferred concentration of active oxygen is below 0.004% by volume.

[0026] In the irradiation step, the ionizing radiation should have sufficient energy to penetrate the mass of linear polypropylene being radiated. The energy must be sufficient to ionize the molecular structure and to excite atomic structure, but not sufficient to affect atomic nuclei. The ionizing radiation can be of any kind, but the most practical kinds comprise electrons and gamma rays. Preferred are electrons beamed from an electron generator having an accelerating potential of 500-4,000 kilovolts. Satisfactory results are obtained at a dose of ionizing radiation of 1-9 megarads (0.01-0.09 MGy), preferably 3-8 megarads (0.03-0.08 MGy), delivered generally at a dose rate of 1-10,000 megarads per minute (0.01-100 MGy/min), and preferably 18-2,000 megarads per minute (0.18-20 MGy/min).

[0027] The term "rad" is usually defined as that quantity of ionizing radiation that results in the absorption of 100 ergs of energy per gram (0.01 J/kg) of irradiated material, regardless of the source of radiation. As far as the instant invention is concerned, the amount of energy absorbed by the polypropylene when it is irradiated is not determined. However, in the usual practice of the process energy absorption from ionizing radiation is measured by the well known conventional dosimeter, a measuring device in which a strip of fabric containing a radiation sensitive dye is the energy absorption sensing means. Hence, as used in this specification the term "rad" means that quantity of ionizing radiation resulting in the absorption of the equivalent of 100 ergs of energy per gram (0.01 J/kg) of the fabric of a dosimeter placed at the surface of the polypropylene being irradiated, whether in the form of a bed or layer of particles, or a film, or a sheet.

[0028] The second step of the process of this invention should be performed in a period of time generally in the range from one minute to one hour, and preferably 2-30 minutes. A minimum time is needed for sufficient migration of polypropylene chain fragments to free radical sites and for combination thereof to reform complete chains, or to form long branches on chains. A radical migration time less than one minute, for example, about a half minute, is within the broader concepts of this invention, but is not preferred because the amount of free-end long chain branching is quite low.

[0029] The final step of the process, the free radical deactivation or quenching step, can be performed by the application of heat or by the addition of an additive that functions as a free radical trap, such as, for example, methyl mercaptan.

[0030] In one embodiment of the process the application of heat comprises extruding the irradiated polypropylene at about 200°C. At this temperature the irradiated polypropylene is melted. As a result, quenching of the free radicals is substantially complete. In this embodiment, prior to the extrusion or melt compounding, the irradiated polypropylene can be blended with other polymers, for example, linear polypropylene, if desired, and additives such as, for example, stabilizers, pigments and fillers. Alternatively, such additives can be incorporated as a side stream addition to the extruder.

[0031] In another embodiment of the inventive process the application of heat is achieved by introducing the irradiated polypropylene into a fluidized bed in which the fluidizing medium is, for example, nitrogen or other inert gas. The bed is established and maintained in a temperature range of at least 80°C up to 160°C and preferably 140-150°C, with the residence time of the irradiated polypropylene in the fluid bed being from 3 minutes to 15 minutes, with about 10 minutes being optimum.

[0032] The product thus obtained is a normally solid, gel-free, polypropylene characterized by strain hardening.

[0033] The process of the invention is performed on a continuous basis. In one continuous embodiment of the process the finely divided linear polypropylene either with or without the preparation step, depending on its active oxygen content, is layered on a traveling belt in the required environment. The thickness of the layer depends on the desired extent of penetration of the ionizing radiation into the layer and the proportion of linear polypropylene desired in the final end product. The speed of travel of the traveling belt is selected so that the layer of finely divided polypropylene passes through the beam or beams of ionizing radiation at a rate to receive the desired dose of ionizing radiation. After having received the required dose of ionizing radiation, the irradiated layer can be left on the traveling belt in said environment for the period of time for free-radical migration and combination to occur, and then removed from the belt, and introduced into an extruder operated at a melt temperature of the irradiated polypropylene, or, in another specific embodiment introduced into a heated bed of particles of irradiated polypropylene fluidized with nitrogen or other inert gas. In either embodiment, the irradiated polypropylene after at least substantially all of the free radicals therein are deactivated is discharged into the atmosphere and quickly cooled to room temperature. In another embodiment, the irradiated polypropylene is discharged from the belt and conveyed in the required environment to a holding vessel, the interior of which has the required environment, and held in the vessel to complete the requisite free radical migration time. The irradiated polypropylene then is introduced into an extruder operated at a melt temperature of the irradiated polypropylene or is introduced into a heated, inert gas fluidized bed of irradiated polypropylene particles, and, after quenching of the free radicals, the irradiated polypropylene is discharged into the atmosphere.

[0034] This invention in still another aspect comprises the extensional flow use of the strain hardening polypropylene of this invention. Extensional flow occurs when the polypropylene in the molten condition is pulled in one or more

directions at a rate faster than it would normally flow in those directions. It happens in extrusion coating operations in which a melted coating material is extruded on to a substrate such as a moving web of paper or metal sheet, and the extruder or substrate is moving at a higher rate than the extrusion rate. It takes place in film production when the molten film material is extruded and then stretched to the desired thinness. It is present in thermoforming operations in which a molten sheet is clamped over a plug mold, vacuum is applied and the sheet is pushed into the mold. It occurs in the manufacture of foamed articles in which molten polypropylene is expanded with a foaming agent. The strain hardening polypropylene of this invention is particularly useful as part of or, particularly in the case of strain hardening, predominantly isotactic, semi-crystalline polypropylene, substantially all of the molten plastic material used in these and other melt processing methods (for example, profile extrusion, as in the melt spinning of fibers) for making useful articles. In the case of the strain hardening amorphous polypropylene of this invention, it is particularly useful when blended with normally solid, predominantly isotactic, semi-crystalline linear polypropylene for use in melt processing and other operations for making useful articles.

[0035] The best mode now contemplated of carrying out the invention is illustrated by the accompanying drawings which form a material part of these disclosures, and by the following examples.

Brief Description of the Drawings

[0036] In the drawings

Fig. 1 is a schematic flow sheet of a preferred embodiment of a continuous process for converting, for example, normally solid, predominantly isotactic, semi-crystalline, linear polypropylene into a normally solid, gel-free, predominantly isotactic, semi-crystalline polypropylene with strain hardening;

Figs. 2-4 are plots of elongational viscosities versus elongation times of a control sample of a non-irradiated, visbroken, linear polypropylene and of samples of two, free-end long branched polypropylene products obtained by the process of this invention; and

Fig. 5 is a plot of normalized elongational viscosity data versus elongation times at a specific elongation rate with respect to the samples of Figs. 2-4.

[0037] In greater detail, Fig. 1 depicts a fluid bed unit 10 of conventional construction and operation into which finely divided linear polypropylene is introduced by way of conduit 11, nitrogen gas is introduced by way of conduit 13, and from which substantially active oxygen free linear polypropylene is removed by way of a solids discharge conduit 15 which also has a solids flow rate controller 16. The solids discharge conduit 15 leads to a conveyer belt feed hopper 20.

[0038] The conveyer belt feed hopper 20 is a capped structure of conventional design. It is operated so that its interior contains a nitrogen atmosphere. It has a bottom solids discharge outlet through which linear polypropylene particles move and form a layer on the top horizontal run of a conveyer belt 21.

[0039] The conveyer belt 21 is generally horizontally disposed, and continuously moves under normal operative conditions. It is contained in radiation chamber 22. This chamber completely encloses the conveyer belt, and is constructed and operated to establish and maintain a nitrogen atmosphere in its interior.

[0040] In combination with the radiation chamber 22 is an electron beam generator 25 of conventional design and operation. Under normal operative conditions it generates a beam of high energy electrons directed to the layer of linear polypropylene particles on the conveyer belt 21. Below the discharge end of the conveyer belt is a solids collector 28 arranged to receive the polypropylene particles falling off the conveyer belt 21 as it turns to travel to its opposite end. Irradiated polypropylene particles in the solids collector 28 are removed therefrom by a rotary valve or star wheel 29 and delivered thereby to a solids transfer line 30.

[0041] The transfer line 30 leads to a gas-solids separator 31. This unit is of conventional construction and usually is a cyclone type separator. Gas separated therein is removed as by gas discharge conduit 33 while separated solids are discharged therefrom as by a rotary valve or star wheel 32 into a solids discharge line 34. The solids discharge line 34 can lead directly to an extruder hopper 35. However, in the embodiment shown, it leads to a plow blender 36.

[0042] In the embodiment shown, there is provided a hopper 37 for such additives as stabilizers or an additive concentrate consisting essentially of finely divided linear polypropylene (or even the polypropylene of this invention) and additives at greater concentrations than in the final product. The additive hopper 37 preferably is conventional, and preferably is constructed and operated to maintain the contents in a nitrogen atmosphere. The discharge end of the additives hopper 37 empties into a screw feeder 38 which feeds material into an additives transfer line 39 that goes to the plow blender 36. In addition, in the embodiment shown, there is provided a bulk feed hopper 41 in which, for example, finely divided or pelletized linear polypropylene is contained. This hopper is conventional, and it too preferably is constructed and operated to maintain the contents in a nitrogen atmosphere. The bulk feed hopper 41 empties into a screw feeder 42 which feeds a solids transfer line 43 that goes to the plow blender 36. In the plow blender 36, the solids fed into it are blended and then discharged into a blended feed line 45 that empties into the extruder hopper 35.

[0043] The extruder hopper 35, which feeds an extruder 47, is conventional in construction and operation. It too is an enclosed structure adopted for establishing and maintaining a nitrogen atmosphere in its interior. The extruder 47 is of conventional construction, and is operated in normal fashion. The solids in the extruder hopper 35 move therefrom into the extruder which is operated at a rate of extrusion to result in the period of time between irradiation of the polypropylene and its entry into the extruder being sufficient for a significant amount of free-end long chain branches to form. Accordingly, the volume of the extruder hopper 35 is selected to provide, if necessary, the desired amount of hopper storage time to meet this condition. The extruder 47 is designed (length of extruder barrel and screw) and operated at a melt temperature and at a pressure sufficient to maintain the free radical containing polypropylene therein for the amount of time needed to deactivate substantially all of the free radicals present.

[0044] The thus treated, finely divided polypropylene is characterized by being substantially gel-free, predominantly isotactic, semi-crystalline, and substantially branched with free-end long chains of propylene units. It can be used as is, or introduced, for example, directly into a pelletizing and cooling unit 49 and conveyed away therefrom as by solids transport line 50 as solid pellets which can be stored and then used, or used without storage.

Examples 1 and 2

[0045] These examples illustrate the non-linear polypropylene of this invention, and the foregoing preferred embodiment of a process for making it.

[0046] In these examples a finely divided (flake) polypropylene of commerce, having a conventional phenolic antioxidant content of about 0.001% by weight, and characterized by a nominal melt flow rate (dg/min., ASTM Method D 1238, Condition L) of 0.2 and density (g/cm³, ASTM method D 792A-2) of 0.902, is introduced into the fluid bed unit 10 and fluidized with nitrogen for 60 minutes.

[0047] The thus treated polypropylene powder is then dropped into the conveyer belt feed hopper 20 which lays it on the moving 200 mesh (0.074mm) stainless steel conveyer belt 21 to form a bed of polypropylene powder 1.5 cm high and 30.5 cm wide. The bed is passed by the conveyer belt 21 through an electron beam generated by a 2 MeV Van de Graff generator operating at a 250 μ A beam current with a scanned beam width of 40.6 cm at the top surface of the conveyer belt 21. The conveyor belt speeds and resulting absorbed surface doses in these examples are set forth in the following Table I. In addition, the active oxygen content of the environment or atmosphere within the enclosed radiation chamber 22 and in the remaining part of the system comprising the irradiated polypropylene transfer line 30, the solids-gas separator 31, the separator discharge line 34, the blender 36, the blender discharge line 45 and the extruder hopper 35, is established and maintained in each example as indicated also in Table I.

[0048] After irradiation, the polypropylene falls off the end of the conveyer belt 21 into the belt discharge collector 28 and through the rotary valve 29 into the transfer line 30. After separation of gas from the irradiated polymer, the polymer is fed through the separator discharge line 34 into the blender 36. In these examples, a finely divided additive concentrate, consisting essentially of a linear polypropylene (100 parts by weight), conventional phenolic antioxidant (10.1 parts by weight), and calcium stearate (7.0 parts by weight), from the additive hopper 37 is added by way of the additives transfer line 39 to the blender 36 at a rate of 3 parts by weight per 100 parts by weight of the irradiated polymer. The resulting blend is then fed by way of blender discharge line 45 from the blender 36 into the extruder feed hopper 35.

[0049] The extruder 47 is a 6.4 cm barrel diameter single screw Sterling extruder operated at a 245°C set temperature to give a 235°C melt temperature. The pelletizing (valved) die of the pelletizing and cooling unit 49 is adjusted to give a pressure of 70 kg/cm² (6.86MPa). The extruder throughput in each example is regulated to match the throughput of linear polypropylene under the electron beam, and there is no irradiated polymer level maintained in the extruder feed hopper 35. In other words, the extruder 47 in each example is "starve-fed". The extruded strands of product from the die are cooled in water and then cold sliced to form pellets.

[0050] Properties of the end products of Examples 1 and 2 and those of a control, a visbroken linear polypropylene of commerce, are summarized in the following Table I.

TABLE I

Material	Belt Speed cm/min	Hold Time Min.	MFR ^a dg/min	IV ^b dl/gm	η_{sp}^c 10 ⁴ poise (dPas)	M_w^d gm/mole	g/f	ΔE_g kcal/mole (kj/mole)
Control: Visbroken Linear Polypropylene	--	--	4.1	2.36	8	298,000 ^e	--	13.3 (55.7)
Example 1 Product (1 Mrad (0.01MGy), 0.2% by vol. O ₂ in N ₂)	45.7	0.6	3.0	2.21	10	343,000	0.98	--
Example 2 Product (6 Mrad (0.06MGy), 0.004% by vol. O ₂ in N ₂)	7.6	4.3	9.4	--	--	--	--	17.2 (72.0)
Sample A ^h	7.6	4.3	9.5	1.85	4.65	1,250,000	0.32	14.8 (62.0)
Sample B								

^a Melt Flow Rate, ASTM 1238-82 Condition L.

^b Intrinsic Viscosity, J. H. Elliott, et al., (supra).

^c Zero Shear Viscosity, e.g., K. Walters, "Rheometry", Chapman and Hall, London, 1975.

^d Weight Average Molecular Weight, M. L. McConnell, (supra).

^e This M_w was obtained by gel permeation chromatography on a GPC-200 instrument.

^f Branching Index.

^g Flow Activation Energy, W. Philippoff, F. H. Gaskins, J. Poly. Sci., 21, 205-222 (1956).
 $\eta(T)/\eta(T_0) = \sigma T = K \exp (\Delta E/RT)$.

^h Sample A was used for extensional viscosity measurements. Sample B was used for all other measurements. These samples were prepared under identical conditions.

[0051] The elongational properties of the three materials are illustrated in Figs. 2-4, and are compared in Fig. 5.

[0052] More particularly, Figs. 2-4 are plots of elongational viscosity (η_E , poise (dPas)) versus time (seconds) at the elongation rates (sec⁻¹) indicated. These data were obtained on samples of the control, the Example 1 product and of

the Example 2 product with the Rheometrics extensional rheometer (RER-9000) referred to above. In obtaining the data of Figs. 2-4, the samples were elongated to failure, and the type of failure noted. One type of failure is referred to as ductile failure. This is failure by thinning. The other type of failure is failure by fracture or elastic failure. In this kind of failure, the material behaves as though it were brittle, and breaks.

5 [0053] Thus, it will be observed in Fig. 2 that for the visbroken linear polypropylene control, a linear polypropylene, as the molten material is stretched or elongated, the elongational viscosity generally increases with time, but as the point of failure is approached, it decreases to such point, whereat the failure is ductile in character. On the other hand, as shown in Figs. 3 and 4 the free-end long chain branched polypropylene samples on stretching exhibit a general increase in the elongational viscosity with time and, as the point of failure is approached, continues to increase somewhat linearly (Fig. 3) in the case of the polypropylene of Example 1 (low amount of free-end long chain branching), and dramatically (Fig. 4) in the case the polypropylene of Example 2 (high amount of free-end long chain branching). Moreover, as Figs. 3 and 4 indicate, the free-end long chain branched polypropylene of each Example fails by fracture.

10 [0054] The elongational properties of the three materials are compared in Fig. 5 in which the normalized elongational viscosities η_E (elongational viscosity) at an elongation rate of 1.0 sec^{-1} divided by η_0 (zero shear viscosity) at the same test temperature as determined by a Rheometrics mechanical spectrometer as a function of time for each of the materials up to the point of failure are plotted. The resulting curves illustrate dramatically the strain hardening properties of the two embodiments of the free-end long chain branched polypropylene of this invention.

Examples 3 and 4

20 [0055] These examples illustrate a melt processing utility of the free-end long chain branched polypropylene of this invention. In particular, they illustrate the use of the non-linear polypropylene in extrusion coating.

[0056] In these examples the melt flow rates are determined by the procedure of ASTM 1238-Condition L.

25 [0057] The extrusion coating compositions of these examples have this basic formulation:

Components	Parts by Weight
Resin	100
Phenolic Antioxidant	0.1
Calcium Stearate	0.07

30 [0058] The composition of the resin component is identified in Table II. In Examples 3 and 4 the free-end long chain branched polypropylene is made as by the process of Fig. 1 from a finely divided, linear polypropylene of commerce, the intrinsic viscosity of which is 4.7, and having a conventional phenolic antioxidant content of about 0.001% by weight. In making the branched polypropylene of these Examples, the electron beam dosage is 8 megarads, the molecular oxygen content of the environment of the system is about 0.1% by volume, and the period of time between irradiation and quench is about 5.5 minutes. The branching index of the resin is typically 0.33. The free-end long chain branched resin typically has a melt flow rate of about 34 dg/min.

40 [0059] The linear polypropylene of Example 4 is a conventional pelletized, linear polypropylene of commerce, the melt flow rate of which is 45 dg/min. It too typically has a conventional phenolic antioxidant at about 0.1% by weight of the polypropylene.

45 [0060] The added antioxidant in each example is a suitable conventional phenolic antioxidant.

[0061] The composition of each example is made by blending the components thereof.

[0062] To use the compositions of the two examples, they are melt extruded through a sheeting die onto a relatively moving substrate such as, for example, paper, metal, or the like.

50 [0063] Typical results are illustrated by the data set forth in Table II. The results were obtained by extruding the compositions set forth in Table II through a 6.35 cm Davis-Standard extruder with a barrel length to diameter ratio of 26:1 and a screw of the metering type with 5 compression flights and 13 metering flights, into a center fed, key hole type, 40.6 cm wide Egan die. The composition in each case was extruded onto a moving substrate just prior to the substrate entering the nip between a chill roll and a nip roll. The following conditions applied for each composition in Table II:

55 Barrel Temperatures: 204°C, 260°C, 288°C, 304°C, 304°C
 Adapter Temperature: 321°C
 Die Temperature: 321°C
 Air Gap: 8.9 cm.

Chill Roll Temperature: 16°C
 Nip Pressure: 13 kg/cm² (1.27MPa)
 Substrate: 13.6 kg/ream (500 sheets, 61 cm x 91.4 cm) unbleached kraft paper
 Linear Speed Range of Takeup System: 30 m/min - 305 m/min
 Extrusion Rate: 36.3 kg/hr.

TABLE II

	Example 3	Example 4	
Resin	Free-End, Long Chain Branched Polypropylene	Example 3 Polypropylene (30% by weight) Linear Polypropylene (70% by weight)	Comparison Conventional Linear Polypropylene
Melt Flow Rate (dg/min)	34	47	35
Max. Coating Speed (m/min.)	213	244	107
Neck-In* (cm)	2.5	3.8	15.5

*Neck-in is the difference between the die width and the final coat width in the substrate.

[0064] As can be seen, the maximum coating speed of the linear polypropylene, is quite low, and the neck-in exhibited by this resin is excessive. Also, it was found that at speeds in excess of the maximum coating speed, draw resonance and then failure of the coating composition occurs.

[0065] As further can be seen, the extrusion coating performance of the polypropylene of this invention, Example 3, is superior to that of the linear polypropylene. The neck-in of the coating composition of this invention is one-sixth that of the coating composition in which the resin component is linear polypropylene. Also, the maximum coating speed attained by the coating composition of this invention is twice that attained by the control.

[0066] The coating composition of Example 4 also exhibits good extrusion coating performance. The neck-in of it is about one-fourth the neck-in of the comparison coating composition, while the maximum coating speed is more than twice that of the comparison coating composition. Blending of the free-end long chain branched polypropylene of this invention with another linear polypropylene of commerce significantly improves the extrusion coating performance of that linear polypropylene.

Example 5

[0067] This example illustrates the use of the free-end long chain branched polypropylene of this invention in air-quenched tubular blown film.

[0068] The composition of this example has this formulation:

	Parts by Weight
Linear Polypropylene (Melt Flow Rate = 7.0-9.0 dg/min.)	90
Free-End Long Chain Branched Polypropylene (g' = 0.33)	10
Antioxidant	0.1

[0069] The free-end long chain branched polypropylene is one made according to the process of Example 1 starting with a linear polypropylene of commerce, the I.V. of which is 4.7, and which typically has a conventional phenolic antioxidant at a concentration of about 0.001% by weight. In the process the linear polypropylene is radiated with an electron beam for a total dosage of 8 megarads (0.08 MGy), the environment from radiation to quenching contains 0.1% by volume of molecular oxygen, and the total time of the radiated material in the environment from radiation to quenching is 5.5 minutes.

[0070] The linear polypropylene component of the composition of this example typically has a conventional phenolic antioxidant content of about 0.001% by weight of the polypropylene.

[0071] The added antioxidant of the composition is a conventional phenolic antioxidant.

[0072] The composition of this example is prepared by blending the components. Typically, the composition, a resin

blend, has a final melt flow of 8.6 dg/min.

[0073] Typical results achieved in using this composition to make blown film are set forth in the following Table III. These results were actually obtained with a modified Chi Chang water-quenched blown film line comprising a 50 mm extruder with a barrel length to diameter ratio of 26:1, and a 100 mm diameter annular die without the usual water ring, but with a larger capacity blower connected to the air ring. The air ring was a single lip air ring with a 45° lip angle and located 4.25 cm below the die. The gap of the air ring was adjustable, but was set at 9 mm. The tower height was 1.9 meters. The polished nip rolls were driven by a variable speed motor which allowed the linear take-off speed of the film to be adjusted.

[0074] The data set forth in Table III also include data obtained with a comparison composition consisting of the same linear polypropylene resin and antioxidant as in the sample of composition of this Example. The melt flow rate of the linear polypropylene was 8 dg/min. (ASTM 1238-Condition L).

TABLE III

	Example 5	Comparison Composition
Processing Temperature (°C)	210	200
Q (kg/hr)	16.8	14.4
Drawdown Ratio MD/CD	7.6/2.7	6.7/2.7
Average Thickness (mm) MD/CD	0.036/0.037	0.039/0.042
Coefficient of Variation of % Thickness MD/CD	2.4/6.0	7.6/23.6
Frostline Position (cm)	22.35	31.75
Haze (%)	17.8	58.2
Gloss (%)	34.8	16.9

[0075] The comparison composition could not be processed on the film line at temperatures above 200°C. Moreover, as can be seen in the table, the film produced from the comparison composition at 200°C had poorer film uniformity, based on the coefficient of variation of thickness, than film produced from the Example 5 composition. On the other hand, the Example 5 composition processed easily at 210°C and gave film with improved gauge control. The haze value of the film of the Example 5 composition is much lower than that for the film of the comparison composition. Also, the film gloss in the case of the Example 5 composition is approximately twice that of the film of the comparison composition.

[0076] Furthermore, the Example 5 composition formed a bubble with a shorter neck and with the frost line closer to the air ring than the bubble formed by the comparison composition. Moreover, the bubble formed by the Example 5 composition was more stable.

Example 6

[0077] This example illustrates the use of the free-end long chain branched polypropylene of this invention in thermoforming.

[0078] The composition of this example comprises:

	Parts by Weight
Commerical impact resin	100.0
Free-end long chain branched polypropylene	42.8
Antioxidant	0.2
Calcium stearate	0.1

[0079] The commercial impact resin consists of a polymeric product formed by the sequential polymerization of propylene and ethylene, and a conventional phenolic antioxidant at about 0.1% by weight of the resin. It has an ethylene unit content of about 6.0-7.5, and the nominal melt flow rate (ASTM 1238, Condition L) is about 0.4 dg/min.

[0080] The free-end long chain branched polypropylene is one prepared as by the process of Example 1 from linear polypropylene, the intrinsic viscosity of which is 4.7, and typically having a conventional phenolic antioxidant content of about 0.1% by weight of the linear polypropylene. The radiation is by an electron beam, the dosage is 6 megarads (0.06 MGy), the controlled environment contains 0.004% by volume molecular oxygen, and the hold time in the environment between irradiation and quench is about 4.3 minutes. The melt flow rate (ASTM 1238, Condition L) of the free-end long chain branched polypropylene is about 8-10 dg/min, and its branching index g' is 0.3.

[0081] The additional antioxidant is a mixture of conventional phenolic antioxidant and a conventional phosphite heat stabilizer.

[0082] The composition of the formulation is prepared by blending the components thereof in a Henschel mixer for 2 minutes at high speed, and then for 1 minute at low speed. The blended material is then fed into a single screw compounding extruder. The extruder is set at the following conditions:

Extruder barrel temperature	
Zone 1	204°C
Zones 2-5	232°C
Adapter temperature	221°C
Die temperature	232°C
Screw speed	110 rpm
Screw diameter	6.4 cm
Length/diameter ratio	24/1
Screen pack	60/100/60 U.S. mesh size (0.25/0.15/0.25mm)

[0083] In combination with the extruder is a pelletizing die having 10 holes of 4.8 mm diameter each. The molten "strands" that exit the die are cooled in a water bath and cold cut into small cylindrical pellets that are dried and collected.

[0084] The blend is subsequently formed into a sheet having a thickness of 0.76 mm and a width of 20.3 mm by extrusion from a single screw extruder with a 25.4 cm sheet die and in combination with a bank of chill rolls. The following sheet formation conditions are used:

Extruder barrel temperature	
Zones 1-3	232°C
Adapter temperature	232°C
Die temperature	232°C
Chill roll temperature	79.4°C
Die opening	1.0 mm
Screw speed	50 rpm
Screw diameter	5.1 cm
Length/diameter ratio	24/1
Screen pack	60/100/60 U.S. mesh size (0.25/0.15/0.25mm)

[0085] The molten web that exits the sheet die is cooled, polished by the chill rolls, and collected.

[0086] The sheet thus formed is used in conventional thermoforming operations.

[0087] Typical results achieved in such operations are exemplified by the following actual data obtained as follows.

The data were obtained with a thermoformer that is a Comet Industries Lab Master equipped with a plug-dish mold for one run and a plug margarine tub mold for another run. Dishes formed in the plug-dish mold were used to measure the thickness of the part at a constant draw-down ratio, and tubs formed in the margarine tub mold were used to measure part thickness at different draw-down ratios. The following thermoforming conditions were used.

Oven heater temperature	316°C
Vacuum	660 mm Hg (88 kPa)
Heating time	varied
Drape delay time	1 second
Drape return time	30 seconds

[0088] A 15.2 cm x 15.2 cm x 0.76 mm section of sheet was placed in a clamping frame and was transported to an oven equipped with infra-red ceramic heaters. After a specified time, the clamping frame was returned from the oven and the molten sheet captured by the ascending mold. The molten sheet was forced against the contours of the mold by activation of vacuum. The formed part was held in the mold until it had cooled, and then was subsequently removed.

[0089] Various heating times were employed and after each cycle, the variation of the thickness of each part was determined. After several cycles had been completed, the data were analyzed and the heating time at which the smallest variation occurred was then determined by further experimentation. The variation at this optimum heating time was recorded as the optimum thickness variation for the composition.

[0090] The thickness of the dishes was measured along the side wall in the circumferential direction, and that of the margarine tubs was measured from the flange down to the base.

[0091] The sheet's resistance to sag over extended heating times was determined by placing the ends of a 40.6 cm x 20.3 cm x 0.76 mm section of sheet in the clamping frame, transporting it to the oven, and recording the time required for the sheet to sag a distance of 7.6 cm below the plane of the clamping frame. The results are shown in the following table which includes data obtained with a comparison composition consisting of the same impact resin, antioxidant and calcium stearate at the same parts by weight as in the formulation of the Example 6 composition.

Table IV

Composition	Optimum Thickness Variation (%)		7.6 cm Sag Time (seconds)
	Dish	Margarine Tub	
Example 6	24	57	120
Comparison Composition	31	60	72

[0092] The data show that the free-end long chain branched polypropylene of this invention is effective in improving the thermoforming properties of commercial impact resin.

[0093] Hence, the free-end long chain branched polypropylene of this invention has utility in melt processing operations to form useful articles. Indeed, the polypropylene of this invention is useful in all melt processing operations in which a polypropylene of enhanced melt strength is desired.

[0094] The expression "consisting essentially of" as used in this specification excludes an unrecited substance at a concentration sufficient to substantially adversely affect the essential properties and characteristics of the composition of the matter being defined, while permitting the presence of one or more unrecited substances at concentrations insufficient to substantially adversely affect said essential properties and characteristics.

Claims

1. Gel-free thermoplastic polypropylene, which has an intrinsic viscosity of at least 0.8 dl/g measured in decahydro-

naphthalene at 135°C, a branching index of less than 1, and which has strain hardening elongational viscosity, the branching index being defined by the equation:

$$g' = \frac{[\text{IV}]_{\text{Br}}}{[\text{IV}]_{\text{Lin}}} \quad \text{Mw}$$

in which g' is the branching index, $[\text{IV}]_{\text{Br}}$ is the intrinsic viscosity of the gel-free polypropylene, and $[\text{IV}]_{\text{Lin}}$ is the intrinsic viscosity of linear polypropylene having substantially the same weight average molecular weight as the gel-free polypropylene, and strain hardening elongational viscosity being defined as meaning that, as said gel-free polypropylene in the molten state at a test temperature is drawn at a constant rate from a fixed point, the elongational viscosity increases until breaking of the elongated melt, and said breaking is by fracture.

2. Predominantly isotactic, semi-crystalline polypropylene according to Claim 1.
3. Polypropylene according to Claim 2 in which the branching index is less than 0.9.
4. Polypropylene according to Claim 3, having an intrinsic viscosity of at least 1 dl/g measured in decahydronaphthalene at 135°C and a branching index of 0.2-0.4.
5. A continuous process for making gel-free polypropylene having strain hardening elongational viscosity from amorphous to predominantly crystalline solid polypropylene without strain hardening elongational viscosity, strain hardening elongational viscosity being defined as meaning that, as said gel-free polypropylene in the molten state at a test temperature is drawn at a constant rate from a fixed point, the elongational viscosity increases until breaking of the elongated material, and said breaking is by fracture, which process comprises continuously:
 - (1) feeding amorphous to predominantly crystalline solid polypropylene without strain hardening elongational viscosity, to an environment in which the active oxygen concentration is established and maintained at less than 15% by volume of said environment;
 - (2) irradiating said polypropylene in said environment with high energy ionizing radiation at a dose rate from 1 to 1×10^4 Mrad/min (0.01 to 100 MGy/min) until substantial chain scission of the amorphous content of the polypropylene has occurred without causing gelation of the polypropylene;
 - (3) maintaining the thus irradiated polypropylene in such an environment until significant formation of long chain branches has occurred;
 - (4) then treating the irradiated polypropylene while in such environment to deactivate substantially all of the free radicals present in the irradiated polypropylene; and
 - (5) removing said irradiated polypropylene from said environment.
6. A process according to Claim 5 in which said amorphous to predominantly crystalline polypropylene is a gel-free, predominantly isotactic, semi-crystalline polypropylene.
7. A process according to Claim 5 or 6 characterised in that the intrinsic viscosity of said semi-crystalline polypropylene is 1-25 dl/g.
8. A process according to Claim 6 characterised in that the semi-crystalline polypropylene is in finely divided particle form.
9. A process according to Claim 6 characterised in that, prior to irradiation, said semi-crystalline polypropylene is established and maintained in said reduced active oxygen environment.
10. A process according to any one of Claims 5 to 9 characterised in that the active oxygen of said environment is

below 0.004% by volume.

11. A process according to any one of Claims 5 to 10 characterised in that the high energy ionizing irradiation is an electron beam.
12. A process according to any one of Claims 5 to 11 characterised in that the absorbed dose of high energy ionizing radiation is 1 to 9 Mrad (0.01-0.09 MGy).
13. A process according to any one of Claims 5 to 12 characterised in that the period of time of step (3) is in the range from one minute to one hour.
14. A process according to any one of Claims 5 to 13 characterised in that step (4) is performed by melting the irradiated polypropylene.
15. Use of predominantly isotactic, semi-crystalline gel-free thermoplastic polypropylene, which has an intrinsic viscosity of at least 0.8 dl/g, measured in decahydronaphthalene at 135°C, a branching index of less than 1, and strain hardening elongational viscosity (as defined in Claim 1), the branching index being defined by the equation:

$$g' = \frac{[IV]_{Br}}{[IV]_{Lin}} \quad | \quad Mw$$

in which g' is the branching index, $[IV]_{Br}$ is the intrinsic viscosity of the gel-free polypropylene, and $[IV]_{Lin}$ is the intrinsic viscosity of linear polypropylene having substantially the same weight average molecular weight as the gel-free polypropylene, for extrusion coating of articles.

16. Use of predominantly isotactic, semi-crystalline gel-free thermoplastic polypropylene, having the properties defined in Claim 15, for the production of propylene polymer film.
17. A melt processing method for making useful articles from predominantly isotactic, semi-crystalline gel-free thermoplastic polypropylene, having the properties defined in Claim 15.
18. A method of applying a coating to a substrate, which comprises extruding onto said substrate predominantly isotactic, semi-crystalline gel-free thermoplastic polypropylene, having the properties defined in Claim 15.
19. A method for making blown film in which predominantly isotactic, semi-crystalline gel-free thermoplastic polypropylene, having the properties defined in Claim 15, is extruded into a tube that sequentially is blown into a bubble.

Patentansprüche

1. Gelfreies, thermoplastisches Polypropylen, das eine innere Viskosität von wenigstens 0,8 dl/g (gemessen in Decahydronaphthalin bei 135°C) aufweist, einen Verzweigungsindex von weniger als 1 hat und eine Kaltverfestigungs-Streckviskosität aufweist, wobei der Verzweigungsindex durch die Gleichung

$$g' = \frac{[IV]_{Br}}{[IV]_{Lin}} \quad | \quad Mw$$

definiert wird, wobei g' der Verzweigungsindex $[IV]_{Br}$ die innere Viskosität des gelfreien Polypropylen und $[IV]_{Lin}$ die innere Viskosität von linearem Polypropylen ist, das im wesentlichen den gleichen Mittelwert der relativen Molekülmasse aufweist wie gelfreies Polypropylen, und die Kaltverfestigungs-Streckviskosität derart definiert ist, daß,

wenn das gelfreie Polypropylen in geschmolzenem Zustand bei einer Testtemperatur bei konstanter Geschwindigkeit von einem festen Punkt aus gestreckt wird, die Streckviskosität ansteigt bis zum Bruch der gestreckten Schmelze, und dieser Bruch eine Fraktur ist.

- 5 2. Überwiegend isotaktisches, halbkristallines Polypropylen nach Anspruch 1.
3. Polypropylen nach Anspruch 2, bei dem der Verzweigungsindex geringer ist als 0,9.
4. Polypropylen nach Anspruch 3, das eine innere Viskosität von wenigstens 1 dl/g (gemessen in Decahydronaphtalin bei 135°C) und einen Verzweigungsindex von 0,2-0,4 aufweist.
- 10 5. Kontinuierliches Verfahren zum Herstellen von gelfreiem Polypropylen mit einer Kaltverfestigungs-Streckviskosität von amorphem bis überwiegend kristallinem festen Polypropylen ohne Kaltverfestigungs-streckviskosität wobei die Kaltverfestigungs-Streckviskosität derart definiert ist, daß, wenn das gelfreie Polypropylen in geschmolzenem Zustand bei einer Testtemperatur bei konstanter Geschwindigkeit von einem festen Punkt aus gestreckt wird, die Streckviskosität ansteigt bis zum Bruch der gestreckten Materials, und dieser Bruch eine Fraktur ist und das Verfahren umfaßt;
15
(1) kontinuierliches Zuführen von amorphem bis überwiegend kristallinem Polypropylen ohne Kaltverfestigungs-Streckviskosität in eine Umgebung, in der die aktive Sauerstoffkonzentration bei weniger als 15 Volumen-Prozent dieser Umgebung vorgesehen und beibehalten wird;
20
(2) Bestrahlen des Polypropylens in dieser Umgebung mit hochenergetischer ionisierender Strahlung bei einer Dosisleistung von 1 bis 1×10^4 Mrad/min (0,01 bis 100 MGy/min), bis eine wesentliche Kettenspaltung des amorphen Gehalts des Polypropylen erfolgt ist, ohne daß eine Gelierung des Polypropylen erfolgt;
25
(3) Beibehalten des auf diese Weise bestrahlten Polypropylens in dieser Umgebung, bis eine deutliche Bildung langkettiger Seitenzweige erfolgt ist;
(4) daraufhin Behandeln des bestrahlten Polypropylen in dieser Umgebung, um im wesentlichen alle freien Radikale im bestrahlten Polypropylen zu deaktivieren, und
(5) Entfernen des bestrahlten Polypropylens aus dieser Umgebung.
30
6. Verfahren nach Anspruch 5, bei dem das amorphe bis überwiegend kristalline Polypropylen ein gelfreies überwiegend isotaktisches halbkristallines Polypropylen ist.
7. Verfahren nach Anspruch 5 oder 6, bei dem die innere Viskosität des halbkristallinen Polypropylens 1-25 dl/g beträgt.
- 35 8. Verfahren nach Anspruch 6, bei dem das halbkristalline Polypropylen in Form von fein geteilten Partikeln vorgesehen ist.
9. Verfahren nach Anspruch 6, bei dem vor der Bestrahlung das halbkristalline Polypropylen in der Umgebung mit reduziertem aktiven Sauerstoff vorgesehen und beibehalten wird.
10. Verfahren nach einem der Ansprüche 5 bis 9, bei dem der Gehalt an aktivem Sauerstoff der Umgebung unter 0,004 Volumen-Prozent liegt.
- 45 11. Verfahren nach einem der Ansprüche 5 bis 10, bei dem die hochenergetische ionisierende Strahlung durch einen Elektronenstrahl erfolgt
12. Verfahren nach einem der Ansprüche 5 bis 11, bei dem die absorbierte Dosis hochenergetischer ionisierender Strahlung 1 bis 9 Mrad (0,01-0,09 MGy) beträgt.
- 50 13. Verfahren nach einem der Ansprüche 5 bis 12, bei dem die Zeitdauer des Arbeitsschrittes (3) im Bereich von einer Minute bis einer Stunde liegt.
14. Verfahren nach einem der Ansprüche 5 bis 13, bei dem der Schritt (4) durch Schmelzen des bestrahlten Polypropylen erfolgt.
- 55 15. Verwendung eines überwiegend isotaktischen, halbkristallinen, gelfreien, thermoplastischen Polypropylens, das

eine innere Viskosität von wenigstens 0,8 dl/g (gemessen in Decahydronaphtalin bei 135°C) aufweist, einen Verzweigungsindex von weniger als 1 hat und eine Kaltverfestigungs-Streckviskosität gemäß Anspruch 1 aufweist, wobei der Verzweigungsindex durch die Gleichung

$$g' = \frac{[\text{IV}]_{\text{Br}}}{[\text{IV}]_{\text{Lin}}} \quad \text{Mw}$$

definiert wird, wobei g' der Verzweigungsindex, $[\text{IV}]_{\text{Br}}$ die innere Viskosität des gelfreien Polypropylen und $[\text{IV}]_{\text{Lin}}$ die innere Viskosität von linearem Polypropylen ist, das im wesentlichen den gleichen Mittelwert der relativen Molekülmasse aufweist wie gelfreies Polypropylen, das für die Extrudierbeschichtung von Gegenständen verwendet wird.

16. Verwendung eines überwiegend isotaktischen, halbkristallinen, gelfreien, thermoplastischen Polypropylen, das die Eigenschaften nach Anspruch 15 aufweist, für die Herstellung eines Propylenpolymerfilmes.
17. Schmelzverfahren zum Herstellen Gebrauchsgegenständen aus überwiegend isotaktischem, halbkristallinem, gelfreiem, thermoplastischem Polypropylen, das über die Eigenschaften gemäß Anspruch 15 verfügt.
18. Verfahren zum Aufbringen einer Beschichtung auf ein Substrat, das das Extrudieren eines überwiegend isotaktischen, halbkristallinen, gelfreien, thermoplastischen Polypropylen mit den Eigenschaften nach Anspruch 15 auf dieses Substrat beinhaltet.
19. Verfahren zum Herstellen einer Blasfolie, bei dem ein überwiegend isotaktisches, halbkristallines, gelfreies, thermoplastisches Polypropylen mit den Eigenschaften nach Anspruch 15 zu einem Rohr extrudiert wird, das anschließend zu einer Blase geblasen wird.

Revendications

1. Polypropylène thermoplastique exempt de gel, possédant une viscosité intrinsèque d'au moins 0,8 dl/g, mesurée dans le décahydronaphtalène à 135°C, un indice de ramification inférieur à 1, et qui possède une viscosité à l'allongement au durcissement par contrainte, l'indice de ramification étant défini par l'équation :

$$g' = \frac{[\text{IV}]_{\text{Br}}}{[\text{IV}]_{\text{Lin}}} \quad \text{Mw}$$

dans laquelle g' est l'indice de ramification, $[\text{IV}]_{\text{Br}}$ est la viscosité intrinsèque du polypropylène exempt de gel et $[\text{IV}]_{\text{Lin}}$ est la viscosité intrinsèque du polypropylène linéaire ayant pratiquement la même masse moléculaire moyenne en poids que le polypropylène exempt de gel, et la viscosité à l'allongement au durcissement par contrainte étant définie comme signifiant que, lorsque ledit polypropylène exempt de gel, à l'état fondu, à une température d'essai, est étiré à une vitesse constante à partir d'un point fixe, la viscosité à l'allongement augmente jusqu'à la rupture de la masse fondue allongée, et ladite rupture se fait par fracture.

2. Polypropylène semi-cristallin, principalement isotactique, selon la revendication 1.
3. Polypropylène selon la revendication 2, dans lequel l'indice de ramification est inférieur à 0,9.
4. Polypropylène selon la revendication 3, possédant une viscosité intrinsèque d'au moins 1 dl/g, mesurée dans le décahydronaphtalène à 135°C, et un indice de ramification de 0,2-0,4.
5. Procédé continu de fabrication d'un polypropylène exempt de gel ayant une viscosité à l'allongement au durcissement par contrainte, à partir d'un polypropylène solide, amorphe à principalement cristallin, sans viscosité à l'allon-

gement au durcissement par contrainte, la viscosité à l'allongement au durcissement par contrainte étant définie comme signifiant que, lorsque ledit polypropylène exempt de gel, à l'état fondu, à une température d'essai, est étiré à une vitesse constante à partir d'un point fixe, la viscosité à l'allongement augmente jusqu'à la rupture du matériau allongé, lequel procédé comprend les étapes qui consistent à :

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(1) introduire en continu ledit polypropylène amorphe à principalement cristallin sans viscosité à l'allongement par contrainte, dans un environnement dans lequel la concentration en oxygène actif est établie et maintenue à moins de 15 % en volume dudit environnement ;

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(2) irradier ledit polypropylène dans ledit environnement par un rayonnement ionisant haute énergie, à une dose de 1 à 1×10^4 Mrad/min (0,01 à 100 MGy/min), jusqu'à ce que se produise une scission substantielle des chaînes du contenu amorphe du polypropylène sans provoquer la gélification du polypropylène ;

(3) maintenir le polypropylène ainsi irradié dans cet environnement jusqu'à ce qu'il se soit produit une formation significative de ramifications à longues chaînes ;

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(4) traiter alors le polypropylène irradié, toujours dans cet environnement, pour désactiver pratiquement tous les radicaux libres présents dans le polypropylène irradié ; et

(5) retirer en continu ledit polypropylène irradié dudit environnement.

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6. Procédé selon la revendication 5, dans lequel ledit polypropylène amorphe à principalement cristallin est un polypropylène semi-cristallin, exempt de gel, principalement isotactique.

7. Procédé selon la revendication 5 ou 6, caractérisé en ce que la viscosité intrinsèque dudit polypropylène semi-cristallin est de 1-25 dl/g.

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8. Procédé selon la revendication 6, caractérisé en ce que le polypropylène semi-cristallin est sous la forme de particules finement divisées.

9. Procédé selon la revendication 6, dans lequel, avant l'irradiation, ledit polypropylène semi-cristallin est établi et maintenu dans ledit environnement à teneur réduite en oxygène actif.

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10. Procédé selon l'une quelconque des revendications 5 à 9, caractérisé en ce que la teneur en oxygène actif dudit environnement est inférieure à 0,004% en volume.

11. Procédé selon l'une quelconque des revendications 5 à 10, caractérisé en ce que le rayonnement ionisant à haute énergie est un faisceau électronique.

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12. Procédé selon l'une quelconque des revendications 5 à 11, caractérisé en ce que la dose absorbée de rayonnement ionisant à haute énergie est de 1 à 9 Mrad (0,01-0,09 MGy).

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13. Procédé selon l'une quelconque des revendications 5 à 12, caractérisé en ce que la durée de l'étape (3) est dans la gamme d'une minute à une heure.

14. Procédé selon l'une quelconque des revendications 5 à 13, caractérisé en ce que l'on réalise l'étape (4) en faisant fondre le polypropylène irradié.

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15. Utilisation d'un polypropylène thermoplastique, exempt de gel, semi-cristallin, principalement isotactique, possédant une viscosité intrinsèque d'au moins 0,8 dl/g, mesurée dans le décahydronaphtalène à 135°C, un indice de ramification inférieur à 1, et qui possède une viscosité à l'allongement au durcissement par contrainte (telle que définie dans la revendication 1), l'indice de ramification étant défini par l'équation :

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$$g' = \frac{[\text{IV}]_{\text{Br}}}{[\text{IV}]_{\text{Lin}}} \quad \Bigg| \quad \text{Mw}$$

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dans laquelle g' est l'indice de ramification, $[\text{IV}]_{\text{Br}}$ est la viscosité intrinsèque du polypropylène exempt de gel et

$[\text{IV}]_{\text{Lin}}$ est la viscosité intrinsèque du polypropylène linéaire ayant pratiquement la même masse moléculaire moyenne en poids que le polypropylène exempt de gel, pour revêtement par extrusion d'articles.

- 5 16. Utilisation d'un polypropylène thermoplastique, exempt de gel, semi-cristallin, principalement isotactique, ayant les propriétés définies dans la revendication 15, pour la production d'un film de polymère de propylène.
17. Procédé de transformation en fusion pour fabriquer des articles utiles à partir d'un polypropylène thermoplastique, exempt de gel, semi-cristallin, principalement isotactique, ayant les propriétés définies dans la revendication 15.
- 10 18. Procédé d'application d'un revêtement sur un substrat, qui comprend l'extrusion sur ledit substrat d'un polypropylène thermoplastique, exempt de gel, semi-cristallin, principalement isotactique, ayant les propriétés définies dans la revendication 15.
- 15 19. Procédé de fabrication d'un film soufflé, dans lequel un polypropylène thermoplastique, exempt de gel, semi-cristallin, principalement isotactique, ayant les propriétés de la revendication 15, est extrudé en un tube qui est ensuite soufflé en une bulle.

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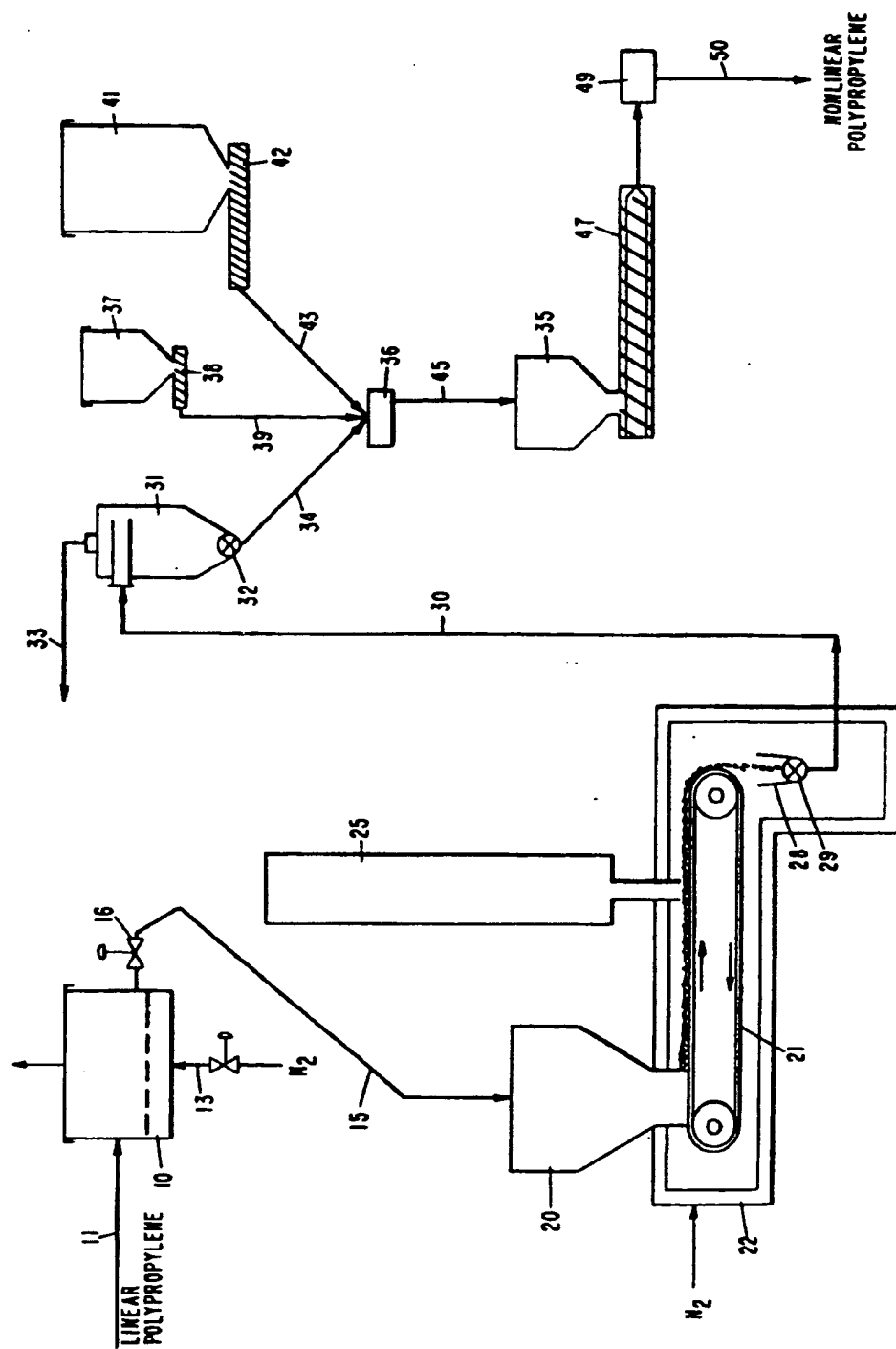
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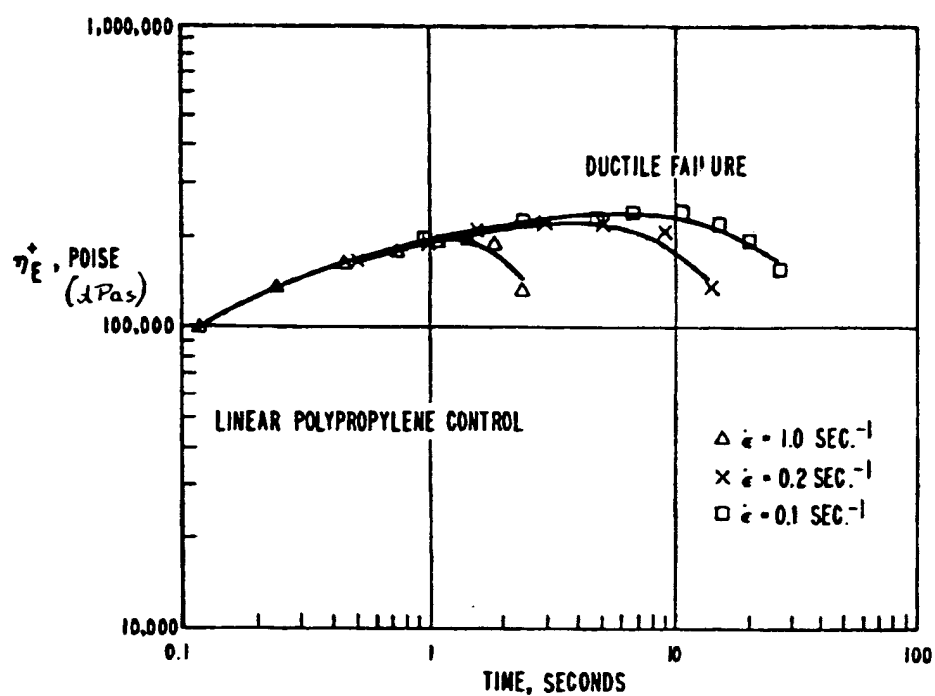


FIG. 2

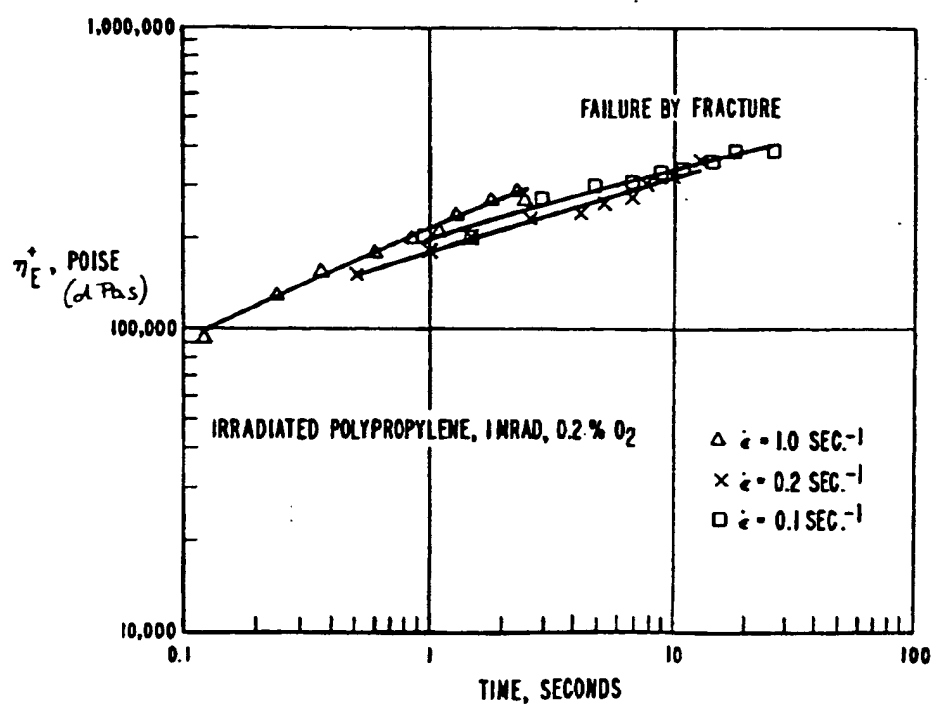


FIG. 3

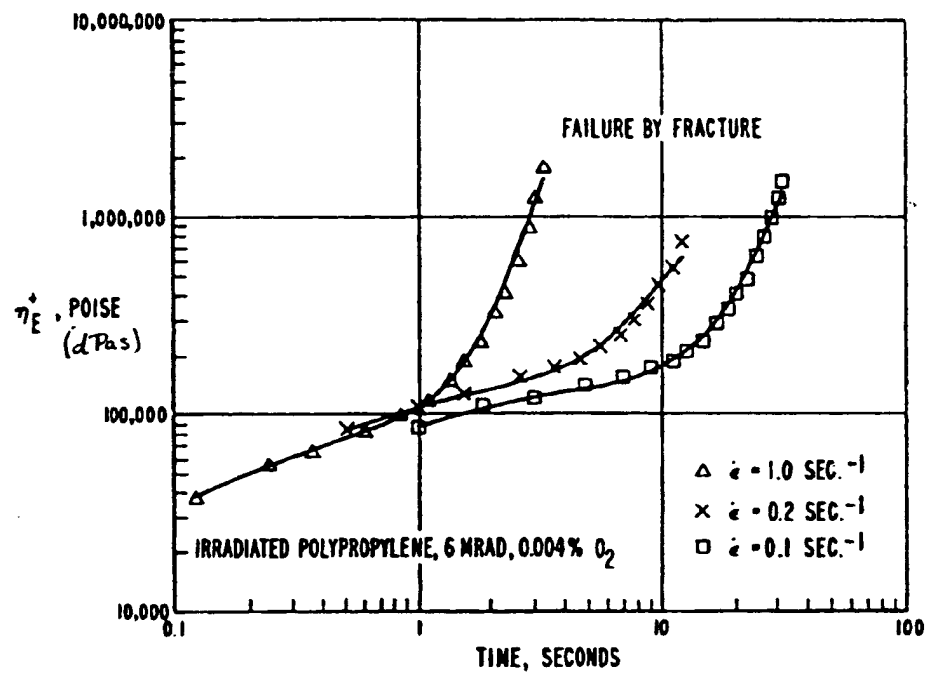


FIG. 4

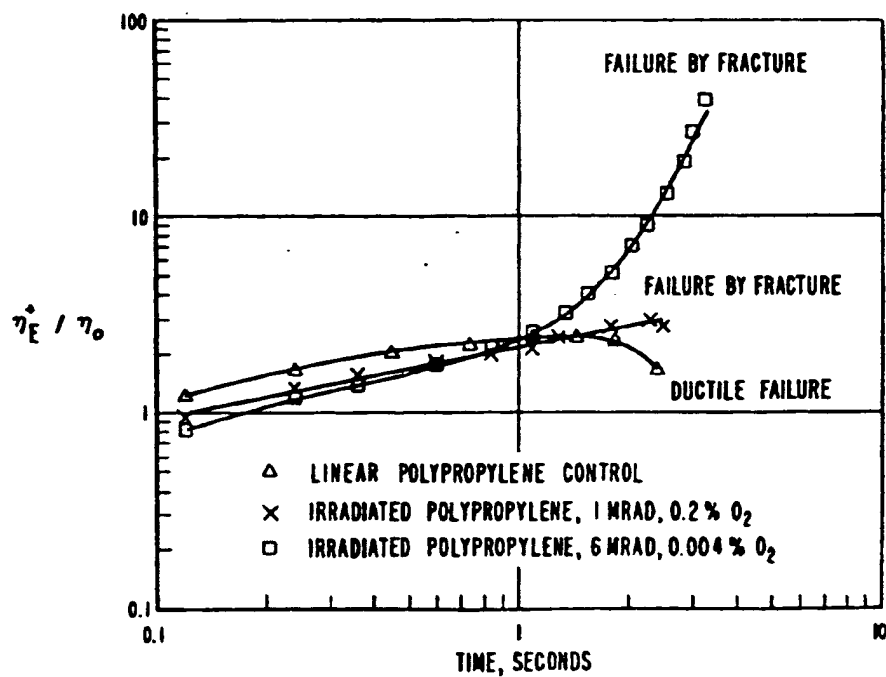


FIG. 5